SEPARATION AND PURIFICATION OF URANIUM AND THORIUM FROM ORGANIC LIQUIDS ON AN ANIONIC EXCHANGE RESIN

by

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NOMENCLATURE

aq	aqueous
Cit	Citrate ion
c.c.	cm^3
DVB	Divinylbenzene
EDTA	ethylenediaminetetra acetic acid
g	acceleration due to gravity
GLX	gel liquid extraction
H.E.T.P.	height equivalent to a theoretical plate expressed in cm. units
I.D.	inside diameter
k	equilibrium constant
k_d	separation factor, $\frac{\text{(gms metal/ml of resin)}}{\text{(gms metal/ml of liquid)}}$
m. moles	millimoles
mg	milligrams
mμ	millimicron
meq	millequivalent
ml	milliliter
M	Molarity, $\frac{\text{(gm moles)}}{\text{liter}}$
N	Normality, $\frac{\text{(equivalents)}}{\text{liter}}$
SDVB	Styrene Divinyl Benzene
TBP	Tributyl Phosphate

INTRODUCTION

The fuels now generally in use in thermal power reactors consist of mixtures of fissile and fertile materials. For example U-235, U-233 and Pu-239 are fissile isotopes which produce neutrons and power through fission. On the other hand, fertile materials such as Th-232 and U-238 absorb some of the neutrons produced in fission to produce more fissionable material and thus replenish some of the fuels consumed in power production.

As fission proceeds in a reactor, however, fission products are also formed, many of these are strong neutron absorbers and are known as reactor or neutron poisons. In order to achieve a high degree of fissile fuel burn up, an economic necessity in power reactor operation, it is necessary to remove the fuel from the reactor, extract fission products from the fissile and fertile materials and then recycle the fuel mixture to the reactor.

The bulk of the power reactor fuels now in use are slightly enriched U-235 (1.5 to 5% U-235) mixed with fertile U-238. There is a growing interest, however, in the so-called thorium-thermal breeder which is fueled with a mixture of fissile U-233 and fertile Th-232. This fuel system is theoretically capable of producing more fuel than is consumed, i.e. for every nucleus of U-233 fissioned, it is possible to produce 1.28 new nuc ei of U-233. Even in these breeders, however, the consumption of nuclear fuel per pass will amount at best to only a few atom percent of the initial loading. Consequently, it will be necessary to recover and separate the unburned fuel and the newly formed fuel from the fission products and

fertile material and then recycle the fuel to the reactor.

The Thorex process (3) is the only one that has been used to any extent to process uranium-thorium fuel elements. In this separation scheme the fuel elements are first dissolved in nitric acid. The separation of uranium, thorium and the fission products is then effected by liquid extraction using tributyl phosphate. It is possible to build selectivity into this procedure so that both uranium and thorium are recovered in highly purified states. Unfortunately this process is also beset with problems such as the loss of extractant through entrainment and emulsification.

Several ion exchange methods are also suitable for the separation of these two elements; however, high purity products in large quantity can be obtained more easily by liquid extraction than by ion exchange.

Small (37) has developed a new process known as gel liquid extraction or GLX to separate several elements from their mixture. The main feature of this scheme is that it incorporates both liquid extraction and ion exchange in a single process. The applicability of such a technique to the separation of uranium and thorium from TBP extractant using a citrate form of an anion exchanger is investigated in this thesis. Methods of uranium and thorium chemical analysis are evaluated and preliminary equilibrium and dynamic elution data are presented.

Uranium-Thorium Separation Principles

Liquid-liquid extraction is commonly employed for the separation of reactor products. Although suitability of several extractants have been studied for the separation of uranium and thorium, tributyl phosphate (TBP)

has been generally adopted because of its superior physical properties (including high flash point, stability against nitric acid and high distribution coefficient). The process employing TBP as extractant for the separation of thorium and uranium is known as the Thorex process; the flow sheet for this process is shown in Figure 1.

Principles of Fission Products Separation From Uranium and Thorium

When an aqueous feed containing uranium and thorium is contacted with TBP, the uranium and thorium are extracted into the organic phase by the formation of certain TBP coordination type complexes according to the following reactions

$$UO_2^{+2}\ (a\ +\ 2\ NO_3^{-1}(a)\ +\ 2TBP(O) \rightleftharpoons UO_2(NO_3)_2\ 2TBP(O)$$

$$Th^{+4}\ (a)\ +\ 4\ NO_3^{-1}\ a)\ +\ xTBP(O \rightleftharpoons Th(NO_{3\ 4}\ x\ TBP(O).$$

where

(a = aqueous phase

(O) = organic phase TBP in a diluent)

x = number of moles of TBP required to form the complex x varies from 1 to 4)

Of the several fission products, the most difficult to remove by TBP extraction are zirconium, niobium, ruthenium and the rare earths. These metals form extractable compounds with TBP according to the following reactions·

For zirconium and niobium,

$$Zr^{+4}(a\ +\ 4NO_3^{-1}\ a)\ +\ 2\ TBP\ O \rightleftharpoons Zr(NO_{3\ 4}\ 2\ TBP\ O\ .$$

For ruthenium,

$$RuNO(NO_{3\ 3}^{-1}\ (a)\ +\ x\ TBP\ O \rightleftharpoons RuNO(NO_3)_3\ x\ TBP(O).$$

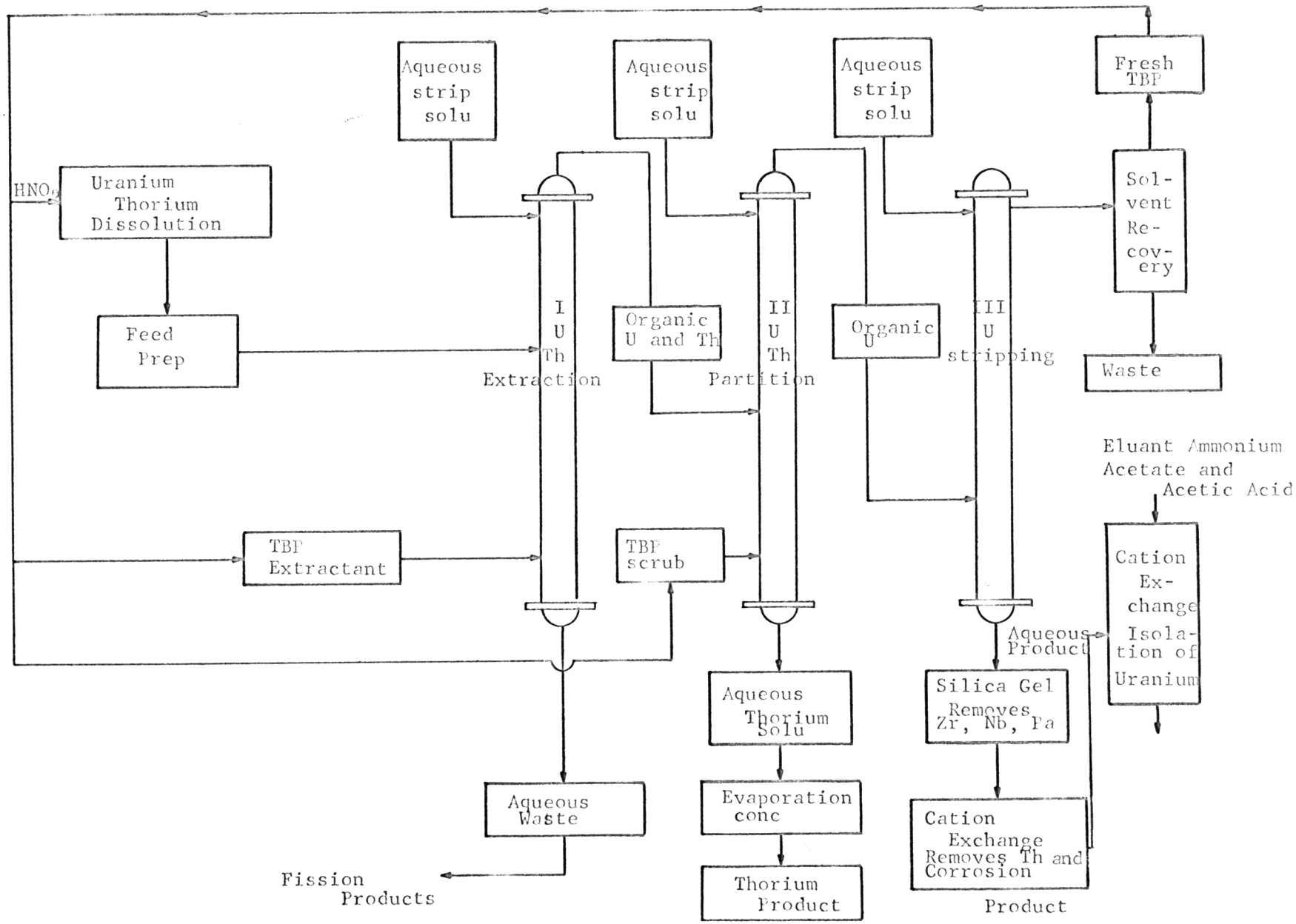

Figure 1 - THOREX PROCESS FLOW DIAGRAM

For the rare earths,

$$M^{+3}\ (a) + 3NO_3^{-1}\ (a) + 3TBP(O) \rightleftharpoons M(NO_3)_3\ 3\ TBP(O).$$

Since all the rare earths under the feed conditions probably exist in +3 valence state, they can be designated by a general symbol M^{+3}.

It is obvious that for effective decontamination from Zr, Nb, Ru and rare earths, the TBP complexes of these metals should not be allowed to form. This is achieved by using an acid deficient solution as the feed to the extraction column. At low acidities zirconium hydrolyses to form zirconyl and $Zr(OH)_2^{+2}$ complexes. In acid deficient aluminum nitrate solutions, the zirconium hydrolysis product is probably present as a non-extractable colloidal substance. Again, in the case of ruthenium and rare earths, low acidity inhibits their extraction by the organic phase. The extraction of these elements can be further retarded by adjusting the TBP content of the organic extract. TBP concentration should be such that it is only in slight stoichiometric excess over that required to extract uranium and thorium. Normally, 30-40% TBP in kerosene diluent is used as the organic extractant.

The Thorex Process

Liquid-liquid extraction columns form the heart of the Thorex process. In column I, thorium and uranium are extracted into the organic phase by the formation of the TBP complex and leave at the top of the column. Aluminum nitrate present in feed and scrub solutions serves as a salting agent. Fission products are held in the aqueous phase and leave column I at the bottom. In column II, separation of thorium and uranium is effected by aqueous scrubbing with dilute nitric acid. Thorium, being less extractable,

enters the aqueous phase. The uranium remains in the organic phase and enters the third column where the uranium is scrubbed out with dilute nitric acid. Uranium collected in the aqueous phase in column III is purified by cation exchange and converted into a suitable compound. The aqueous thorium leaving column II is also generally treated by ion exchange to obtain a purer product. Then the thorium is converted to some chemical form suitable for fuel rod fabrication, e.g. thorium oxide.

The main disadvantage of the thorex process is TBP loss through emulsification and entrainment. In addition, TBP also undergoes slow degradation by hydrolysis. Small concentrations of the hydrolysis products cause a significant increase in the extraction of fission products. This slow hydrolysis of TBP necessitates that the solvent be purified by washing with a sodium carbonate solution and then with dilute nitric acid. This washing procedure further complicates the flow scheme shown in Figure 1.

TBP is also lost due to decomposition by dissolved radioactive materials. The amount of solvent decomposed in unit time is greater the greater the amount of solvent exposed to radiation and the greater the amount of radioactive material present. The inventory of both solvent and radioactive material can be reduced by using compact equipment with high throughput per unit volume.

The GLX Process

In order to overcome or minimize some of the drawbacks of liquid-liquid extraction, Small (37) introduced the concept of incorporating the extractant in a solid form. It is known that co-polymers of polystyrene-divinylbenzene (DVB) swell in water and in several organic solvents forming

a gel-like mass. This gel could then be exploited to support either an organic or aqueous phases in solid form.

Small (37) investigated the suitability of both TBP swollen and water swollen gels for several separation processes. These separation processes, known as gel liquid extraction or GLX processes, were found to be effective and also efficient. The high efficiency is due to the very low H.E.T.P. values (of the order of a few millimeters) that are possible with ion exchange resins. Yet another advantage of the GLX process is that the conditions for mass transfer may be made highly favorable by almost unlimited choice of flow rates, resin particle size and degree of resin cross linking.

If the GLX process were applicable to the separation of uranium and thorium, a considerable simplification in the existing Thorex process could be effected. It was hoped that by incorporating a suitable ion exchange species in the resin and employing a water swollen resin, a high separation factor between uranium and thorium would be achieved. Higher separation factors coupled with the low H.E.T.P. values of ion exchange resins would mean smaller equipment volume with consequent benefits of lowered shielding mass requirements and reduced radioactive induced decomposition of the solvent. Also, assuming the GLX concept were applicable, it would be possible to eliminate at least two pieces of process equipment (Columns II and III shown in Fig. 1). The TBP extractant, containing both uranium and thorium, free from fission products, would be fed immediately to a counter current ion exchanger unit. The separation of uranium and thorium would then be effected in

one process unit employing a suitable eluent. It is anticipated that the products obtained will be sufficiently pure that purification by additional ion exchanger columns will not be necessary.

The principal requirement of any solid-liquid contactor for the type of system under consideration is dependability and compactness. The need for remote operation and maintenance of a radioactive system dictates the use of simp e, rugged equipment with a minimum of moving parts and with little tendency to foul, clog or corrode. The A.E.C.-Higgins (19) contactor or the continuous countercurrent ion exchanger developed at Oregon State University (29) combine high throughput and low theoretical stage height with essentially continuous flow, and hence could be considered for application in GLX processing.

Previous Work on the GLX Concept

In view of the superior properties of TBP noted earlier, Small (37) selected TBP swollen gels for his initial GLX studies. The gel did not contain any exchangeable ion species and acted merely as a support for the TBP phase. Gels were prepared from co-polymers of styrene-divinylbenzene (designated as SDVB). (The percent of DVB used in preparing the resin is indicated by the number following X, thus, SDVB-X4 means that the co-polymer preparation involved the addition of 4% (weight) of DVB.)

Since TBP swollen SDVB polymers are hydrophobic, they tended to agglomerate when placed in water; thus when this material was placed in mass transfer columns it tended to form liquid impermeable beds with poor mass transfer characteristics. This hydrophobic character was overcome by sulphonation of a thin shell surrounding the exterior surface of the resin beads. An additional problem with the SDVB polymers was that

they did not swell readily in TBP and thus the resin's sorption capacity was severely limited. To increase the degree of resin swelling and thus the amount of resin sorbed TBP, a mixture of perchlorethylene and TBP was employed in preparing the swollen gels.

Evaluation of such gels was accomplished by measuring their capacity to extract uranyl nitrate from an aqueous solution. (Water was used as the uranium eluant and was found to remove effectively uranium from the resin.) On the basis of data collected on co-polyomers of different DVB content it was concluded that lower DVB content favored both the uptake of solvent and swelling of the resin with a consequent increase in the amount of uranyl nitrate extracted per gram of gel. The process appeared to be so promising that Small used these gels further to study the separation of (1) ferric nitrate from uranyl nitrate, (2) thorium nitrate from yttrium nitrate and (3) uranyl nitrate from thorium nitrate (37).

As another variation of the GLX process Small employed water swollen resin as the solid phase and the organic solvent as the mobile phase. The resin used in these runs contained a suitable ion exchange species. To introduce a suitable exchangeable ionic species into a SDVB co-polymer, it was first converted to a cation or anion exchanger and then the desired cation or anion was incorporated in the resin by an ion exchange process. In the aqueous media it was also noted that the "swellability" or water uptake of the ion exchange resin again depended inversely on the degree of cross-linkage.

Small reasoned that by choosing a water swollen resin containing an ion exchange species, the selectivity due to extraction could be superimposed on the selectivity due to ion exchange. This coupling of selec-

tivity would lead to a larger overall separation factor and more efficient separation of a mixture. However an attempted separation of a rare earth phosphate using a water swollen Dowex-50 and di (2-ethyl Hexyl) phosphoric acid solvent proved to be inefficient. This failure was due to (1) the low solubility of rare earth phosphates in water, and (2) to a thin film of water around the resin particles which effectively eliminated the contact between the two phases. This latter phenomenon is one of the chief limitations of the GLX process.

In another attempt to separate rare earth elements, Small employed TBP as the organic phase and water swollen Dowex-1 (in nitrate form) as the solid phase. Here the ion exchange function was secondary in that it acted merely as a support for the water phase, although being analogous to a nitrate solution, it exerted a salting out effect on the rare earth nitrates, forcing them into the mobile phase. TBP was also used as an eluent. In this case it was found that a separation of the lighter rare earths was feasible.

With regard to the study presented in this thesis, if the GLX process should prove applicable to the separation of uranium and thorium, then the two scrubbing sections noted in the thorex process flow sheet (see Figure 1) could be eliminated. To eliminate these two process units it would be necessary that the TBP laden organic from the first extraction column be contacted counter currently with a suitable water swollen resin.

REVIEW OF URANIUM-THORIUM CHEMISTRY

A literature study of the chemistry of uranium and thorium revealed that both show a strong tendency for the formation of complex compounds

with the anions of such salts as nitrates, sulphates, fluorides, chlorides and among the organic oxyacids with oxalate, tartrate, citrate and others. In both these types of compounds the co-ordination number of thorium is generally 6 or 8, e.g.,

$$Th(NO_3)_6^{-2} \qquad \text{or} \qquad Th(C_2O_4)_4^{-4}$$

On the other hand uranyl ion exhibits a co-ordination number of 3, 4 or 6, e.g.,

$$UO_2(NO_3)_3^{-1}, \qquad UO_2(NO_3)_4^{-2} \qquad \text{or} \qquad UO_2F_6^{-4}$$

The criterion for choosing an anion exchanger in the present studies was that while thorium and uranium could be adsorbed and recovered from the organic phase by the formation of their anionic complexes, many other metal ions which do not form such complexes could be conveniently separated and eliminated. Also, it was known that certain commercial strong base anion exchange resins show great and at times startling selectivities for complex ions and thus separating metals which exhibit very similar chemical properties can be achieved. Therefore in the present studies Dowex 2-X8, a strong base anion exchanger was selected. The properties of this resin are given in Appendix A.

In separation by anion complex formation, the suitability of a particular anion as the complexing agent depends on the difference in the stability constant of the complexes this ion will form with the two species to be separated. Of the available complexing agents citric acid and ammonium citrate which had proved successful in the separation of rare earth elements (18), appeared promising for the separation of

uranium and thorium (see following section). However since sodium citrate or citric acid, the possible sources of the citrate anion, are insoluble in TBP, citrate complexes of these metals could not be formed in TBP solution. The other alternative was to incorporate the citrate anion in the resin phase.

As a first step in this investigation it was necessary to determine the equilibrium between TBP and water swollen resins for various mole fractions of thorium and uranium. The exchange between the TBP and resin phases could be considered to take place in the following two steps:

(1) Both thorium and uranium, or one of them alone, would be extracted into the water held by the resin. This amounts to scrubbing of the metal rich organic by the water.

(2) Citrate complexes would form in the resin. The separation factor possible in this step depends on the extent of adsorption of the anionic complexes by the resin matrix.

It is rare that complex formation takes place in the resin phase, however, in the uranium case, there is reason to believe that such a phenomenon occurs. It is known that when sulphate form anion exchange resin is brought into contact with uranium aqueous solutions, uranyl ion is adsorbed from solution due to the formation of anionic sulphate complexes although no such complexes existed initially in the solution. The complex formation can be described as follows:

$$UO_2(SO_4) + SO_4^{-2}(R) \rightleftharpoons UO_2(SO_4)_2^{-2}(R)$$

(R) = Resin

No similar example is known to exist in the thorium case. The types of complexes possible, their nature and stability constants for the species citrate anion and thorium and uranyl cations, are discussed briefly in the following sections.

Thorium Citrate Complexes

M. Bobtelsky and B. Graus (4) attempted to determine the solubility, composition and behavior of the various compounds existing between thorium nitrate and citric acid in acid, neutral and alkaline media. They report that on gradual addition of sodium citrate to thorium solution an insoluble white precipitate is obtained. The precipitation is complete at a pH of 1.8 and a 1 to 1 thorium to citrate ratio, 1(Th):1(Cit). On continued addition of sodium citrate, the salt $(ThCit)_n$ dissolves giving (Th_2Cit_3) and the pH rises to 3. At a high pH the soluble (Th_2Cit_3) is believed to form an anionic complex of the type $(Th_2Cit_3)^{-4}$. The anionic complex corresponding to (Th_2Cit_3) is formulated as $(Th(OH)_2Cit_3)^{-3}$. Brown and Rieman (5) also attempted to determine the nature of the thorium citrate complexes using Dowex-50 cation exchanger and diammonium citrate as the eluting agent. From their studies in the pH range 2.1 to 3.47 they arrived at the conclusion that the predominant complex is $ThCit_2^{-2}$.

On the basis of certain pH titration data and studies on strong base anion exchange resin Dowex-1 in citrate form, Li and White (27) postulate the anionic complexes as $Th(Cit^1Cit)^{-3}$ where Cit^1 is the citrate ion with a charge of -4, i.e. one in which the hydroxyl group has been

displaced.

From the foregoing it can be concluded that a wide discrepancy of opinion exists regarding the exact nature of thorium citrate complexes.

Uranium Citrate Complexes

Based on potentiometric studies, Rajan and Martell 33) concluded that uranyl and citrate ions formed polynuclear complexes and the formation constants for these as determined by them are as follows

(1) for monomerization

$$\log k_1 = 7.4 \text{ where } k_1 = \frac{UO_2Cit^{-1}}{(UO_2^{+2})\ (Cit^{-3})}$$

(2) for dimerization

$$\log k_2 = 4.07, \text{ where } k_2 = \frac{UO_2\ {}_2Cit_2^{-2}}{UO_2Cit^{-2}}$$

Feldmann and Neumann 13 found that two citrate complexes of the uranyl ion exist over a pH range of 2.0 to 3.64. A highly associated complex with a molar ratio of unity and a more dissociated complex of ratio 2 1, (UO_2 citrate , was also found.

Feldmann 13 in another publication reports that at pH 3.5 uranium forms a 1 1 dinuclear complex with citrate and at slightly alkaline pH these dimers react completely to form binuclear complexes. Two dimers exist having $\frac{\text{Uranium}}{\text{citrate}}$ group ratios of 3 3 and 3 2. Feldmann (12), in another report, shows that the formation constant for the aqueous reaction

$$2UO_2^{+2} + 2H\ Cit^{-2} \rightleftharpoons [UO_2(OH)HCit]_2^{-2} + 2H^+$$

is $\log k^{\frac{1}{2}} = 3.84$.

Heitner and Bobtelsky 17), based on spectrophotometric and potentiometric studies, report the existence of two complexes, UO_2Cit^{-1} and $(UO_2)_2Cit_3$. The complex UO_2Cit^{-1} exists at a pH below 7 whereas complex $(UO_2)_2Cit_3$ exists between pH 7 and 9. The formation constants of these complexes are log k = 3.03 and 6.06 respectively. At pH 9 the $(UO_2)_2Cit_3$ decomposes and forms a uranium hydroxide precipitate.

Gustafson and Martell 16 , on the basis of non-equilibrium ultracentrifugation studies, support the dimer theory formation giving $UO_2Cit_2^{-2}$ as the correct formula. All the authors studied concur regarding the formation of a complex with $(UO_2$ (Cit = 1 1 in the pH neighborhood of 2-4.

Li and White 27 made several attempts to determine the distribution coefficient between Dowex-1 anion resin (citrate type and uranyl nitrate, sodium citrate solution. In the cases studied, all the uranyl ion was taken up by the resin so that no rational distribution coefficient could be determined.

ELUTION OF URANIUM AND THORIUM FROM RESIN

As part of the equilibration experiments described in this thesis, it was necessary to elute the uranium and thorium loaded resin to obtain an estimate of the amounts of the metals sorbed. The suitability of nitric acid and hydrocholoric acid as eluents was surveyed and the results are presented below.

Hydrochloric Acid as an Eluent

Kraus 25) has investigated the adsorption of Th(IV) and U(VI) on a

strong base anion exchange resin. He found that Th(IV) does not show any adsorption in the HCl concentration range of 0.1 to 12M. The adsorbability of uranium (VI) rises steeply with increasing HCl concentration from K_d = 1 in 1 molar acid to k_d = 1800 near 9 molar HCl. This result is due to the formation of a negatively charged chloride complex of the type $UO_2(Cl)_4^{-2}$. Thorium does not form any such complexes in chloride solutions.

Similar results have been reported by L. R. Bunny (6) et al from their studies on Dowex-2 anion exchange resin. Thorium did not show significant adsorption at any chloride normality and uranium showed maximum adsorption in 8 M HCl. Thus it is expected that concentrated hydrochloric acid would be an excellent eluent for stripping thorium from a uranium-thorium loaded anion exchange resin bed; the uranium would be left behind in the bed and could be stripped out after the thorium was eliminated with dilute HCl.

Nitric Acid as an Eluent

D. J. Carswell (7) has investigated the anion character of thorium in nitric acid solution and determined the distribution coefficient between De-acidite FF (anion exchanger) and Th $(NO_3)_4$ in different concentrations of nitric acid. He found that k_d values ranged from 2 in 2M acid to a maximum of 200 in 8M acid. Similar studies conducted with uranyl nitrates gave k_d values ranging from 4 to 6 for acid concentrations of 2 to 8M. Similar results are reported by F. P. Roberts and R. P. Brauer (34) who used Dowex-1 anion exchange resin; the following table shows their distribution coefficients.

HNO_3(Moles/liter)	2	4	6	8	10
Thorium (IV), k_d	15	50	200	300	200
Uranium (VI), k_d	0.1	3	7	8	4

Studies on Dowex-2 anion resin by L. R. Bunny (6) and others indicated that there is no adsorption of either Th or U(VI) at acid concentrations of less than 1 molar. Both show maximum adsorption near 8M with thorium having a higher distribution coefficient than uranium. The maximum k_d values are 110 for thorium and 8 for uranium.

From the foregoing it is clear that in dilute acid media nitrate complexes of thorium and uranium do not form. Hence dilute nitric acid also could be used to elute thorium and/or uranium complexes from an anion exchanger.

CHEMICAL ANALYSES

Estimation of Thorium

Of the many methods available for the analysis of thorium, the xylinol-orange EDTA volumetric method, the spectrophotometric method using thorin indicator, and the gravimetric method based on flouride precipitation were considered in this study.

The xylinol-orange EDTA method is based on the formation of a 1:1 lemon-yellow colored thorium-EDTA complex. Thorium also forms a red colored weaker complex with the indicator, xylinol orange. The end point in the EDTA analysis is indicated by the color change from red to lemon yellow. The thorium-EDTA complex, however, is pH sensitive and titration is only possible in the pH range of 2 to 3.5. At low pH values, the results for thorium are low, whereas at higher pH values the color change is indistinct. In the present studies, since the elution effluent was reduced from a large volume to a volume of 50 mls, the pH of this concentrated solution was about 1 or less. Hence adjustment by a buffer solution to pH2-3.5 would be required.

In addition to the pH problem, the EDTA method is only useful when the thorium content of the test solution is a few milligrams per ml. The large quantities of thorium present in the experimental solutions of this study would introduce large errors if the EDTA method were applied. Another complication of the EDTA method is introduced when uranium is present. This method can not be easily adapted for the estimation of uranium from the same solution which has been analyzed for thorium. Therefore this method was not considered further.

Spectrophotometric analysis for thorium is based on the formation of a red colored complex when thorin is added to thorium solutions. This colored complex shows maximum adsorbance at a wavelength of 545 mμ and obeys Beer's law in the range of 1 to 10 mgms of thorium per ml. of solution. The procedure to be followed in the spectrophotometric analysis is indicated in Appendix B. This method is best suited for the estimation of thorium in microgram quantities. Since the method is pH sensitive, pH adjustment to 1 before making adsorbancy measurements would be required. Although it is claimed that the spectrophotometric thorium analysis can be carried out in the presence of uranium, experimental results showed that the analysis was not reliable in the presence of variable amounts of uranium and this method was abandoned also.

The gravimetric thorium analysis is based on the formation of insoluble thorium iodate, benzoate, oxalate or flouride. The oxalate and flouride precipitation methods are the most commonly employed. Uranyl ion if present forms a soluble complex and remains in solution. A preliminary check on oxalate and fluoride precipitation methods indicated that both were potentially useful for the thorium determinations to be made during this study.

It is known that thorium oxalate is slightly soluble in acid solutions. Hence it was feared that for acid solutions containing small amounts of thorium, large errors would be incurred if the oxalate method were used. Also, the oxalate precipitation method can not be easily adopted for the estimation of uranium from the same solution. Therefore the flouride precipitation method was finally employed for all thorium analysis work.

It was feared that the high temperatures 800-900°C) required for the ignition of thorium fluoride to the oxide may not be possible with the ordinary burners available in this laboratory. However a few test runs to determine the accuracy of the method indicated that reliable results could be obtained by repeatedly moistening the precipitate with water and igniting it with an available Fisher blast burner.

The filtrate obtained after the precipitation and filtration of thorium fluoride was used for the determination of uranium.

Estimation of Uranium

For experimental samples containing low concentrations of uranium quick estimation of uranium concentration can be accomplished by spectrophotometric methods. Among the various inorganic indicator compounds that are used for the spectrophotometric determination, alkaline peroxide, carbonate and thiocyanate are the most common. Of these, alkaline peroxide is not suitable for the analysis of uranium when thorium too is present in solution. The strongly alkaline solutions used for the formation of the colored complex would precipitate the thorium. Elimination of all thorium from experimental solutions would be necessary if this method were to be successfully adopted.

When dissolved in a sodium carbonate solution, uranyl compounds produce a characteristic yellow color. This color can be used for the determination of uranium by absorbancy measurements made at 320mμ. However the difficult-to-remove nitrate ion interferes with the analysis.

Thiocyanate ion reacts with uranyl ion in acid solution to form a yellow colored complex that absorbs light in the ultraviolet region at

365 mμ to 375 mμ. The method is applicable in the concentration range from 0.2 to 4 mg of uranium per 100 mls of solution. Since the amount of uranium present in the eluent effluent varied from 0 to 200 mgms per 100 m s, the thiocyanate method could not be applied directly in the present studies.

In concentrated solutions uranium can be determined directly by spectrophotometric measurements at 420 mμ without the addition of a color forming reagent. The experimental procedure applicable to concentrated solutions is described in Appendix C. However in many of the elution solutions obtained in this study the uranium content was too low to permit direct application of this method.

The gravimetric method employed in this study for the determination of uranium is based on the precipitation of uranyl ion as ammonium diuranate. The filtrate obtained after the elimination of thorium was converted to ammonium diuranate by NH_4OH addition. The diuranate was separated and ignited and the uranium weighed as U_3O_8. The detailed analytical procedure is indicated in Appendix D.

SYSTEM SELECTED FOR STUDY

Based on the theory and discussion presented above, the following GLX chemical scheme was selected for study. Since uranium and thorium both form anionic complexes with citrate ion and also to exploit the high selectivity exhibited by strong base anion exchangers towards such complexes, Dowex 2-X8 citrate type of water swollen resin was chosen for the study. As previously indicated, 30-40 percent TBP in kerosene diluent is normally employed as the organic extractant in the Thorex

process. Hence it was decided to obtain the data presented here for TBP concentrations of 30 volume percent. Further, to separate only thorium from the loaded resin, it was planned to study the suitability of concentrated HCl as the thorium eluent. Should this prove successful, it was expected dilute nitric or hydrochloric acid could then be used as the eluent to strip uranium from the resin and a complete separation of uranium and thorium would be effected.

PROCEDURE

To determine the feasibility of separating uranium and thorium from the organic extractant, TBP, by contacting with an anion exchanger, it was necessary to determine the equilibrium concentration of uranium and thorium in the resin phase. After equilibration with a TBP solution of a known concentration, uranium and thorium adsorbed by the resin were determined by eluting the loaded resin with dilute nitric acid and analyzing the eluent for both uranium and thorium. The experimental procedure followed is described below.

Dowex 2-X8 form of resin is normally supplied in the chloride or hydroxyl form. The chloride form purchased for this study was converted to the citrate form by "simple" ion exchange. A 4' long 1" I.D. glass column was half filled with water; chloride form resin was slowly introduced from the top so that it settled at the bottom of the tube. Air bubbles and dust particles were removed from the resin particles during this settling process and by subsequent back washing with distilled water. The resin was then contacted with an approximately 2 N. solution

of citrate ion (sodium citrate), siphoned into the column at a rate of 8-10 cc per minute. Flow of citrate solution was stopped when the effluent showed no precipitate of silver chloride when tested with $AgNO_3$. The contents of the column were drained into a beaker, washed several times with distilled water and stored under water. This resin was subsequently used for the equilibration experiments.

The equilibration experiments were conducted in a plexiglass cell with a stainless steel wire mesh partition. A preliminary calculation and test equilibrium run showed that 3-4 gms of wet resin would be adequate for obtaining results of reasonable accuracy, i.e., the quantity of thorium and uranium sorbed by the resin would be such that it could be conveniently detected by a gravimetric analytical method described in the analysis section.

To reduce the data obtained to the basis of mgms of metal sorbed per gram of dry resin, a relation between the weight of wet and dry resin was determined. For this determination, 3 to 4 gms of wet resin was placed in a weighed centrifugation cell. This resin was centrifuged at approximately 300 g's for 8-10 minutes to remove the interstitial water. The cell was again weighed to determine the grams of wet resin. The water held within the resin was then removed by heating the resin to a constant weight at 105°C. This experiment was repeated four times to obtain the average value of grams dry resin/gram wet resin, within $\pm$ 1.7 weight percent.

The concentration of TBP normally used in the Thorex process is between 30-40 volume percent in kerosene. Hence in the present case it

was decided that 30 volume percent TBP would be used as the organic phase. In view of critical ty hazards present in handling highly enriched uranium streams very dilute solutions of uranium are normally handled in the Thorex process. It was found by calculations shown in Appendix F, that the critically safe concentration of enriched (100 percent) uranium (U-233) in TBP solution at infinite volume is of the order of 10 gms liter. Uranium solution strengths of this order were used; the total molarity of uranyl and thorium nitrate was fixed at approximately 10.5 m. moles in 500 mls of TBP solution. The equilibrium data were obtained for 1, 0.8, 0.6, 0.2 and 0 mole fraction of thorium in the uranium-thorium mixture.

For each experiment 3-4 gms of the wet resin was placed in an equilibration cell, centrifuged at 300 g's for 8-10 minutes and then weighed to determine the wet resin weight. A TBP solution of uranium and thorium was next passed through the cell at a rate of 60-70 mls per hour until 500 mls of the solution had passed through the cell (6-7 hours was normally required). A test equilibrium run showed that this volume of organic and this length of time would be sufficient to attain equilibrium. After equilibration the loaded resin was again centrifuged to remove the interstitial organic solution.

Before eluting, the resin was washed with water. During the wash process a mixture of white and yellow precipitate was obtained; it was decided to estimate the thorium and uranium content of this precipitate. Hence the resin was washed free of all the precipitate and the wash solution collected. A few drops of concentrated nitric acid were added to the wash solution and warmed to dissolve the precipitate. The solution was evaporated to dryness and made up to a definite volume of 25 or 50 mls. The uranium and thorium content of this solution was then quantitatively determined.

When the resin in the cell had been washed free of precipitate it was again centrifuged and connected to the lower end of a buret containing the 0.5N nitric acid eluent. It may be noted that dilute HCl could also have been used as the eluent; however since this HCl would corrode the stainless steel wire mesh of the sample cell and thus introduce iron contamination into the cell, nitric acid was selected. The volume of eluent used was sufficient to elute all thorium from the resin phase as tested by thorin indicator. At this point it was also assumed that all uranium was removed. It was found that in each case that approximately 500 cc of the eluent was required. This volume of eluent was reduced to 50 cc by evaporation and the concentrated solution was subsequently analyzed for uranium and thorium.

The suitability of concentrated hydrochloric acid as an eluent for thorium was also studied. As noted above uranium forms chloride complexes in concentrated HCl. The uranium chloride anion complex would be sorbed by an anion exchanger whereas thorium, which does not form such complexes, would not be sorbed by the resin. An aqueous solution of uranyl thorium nitrate at a total molarity of 18.4 millimoles was prepared. The HCl concentration was set at 9 molar and a 250 ml volume of this solution was placed in a buret and subsequently contacted with a known weight of centrifuged resin in a sample cell. The solution flow rate of 60-70 cc per hour as used in the other experiments was again used. The effluent from the resin bed was collected in 50 ml aliquot and each batch was analyzed for uranium and thorium. After the 250 mls of solution had passed through the resin, the resin was centrifuged and eluted with dilute

hydrochloric acid. The sample cells employed in work with HCl were entirely similar to those used for the equilibration experiments, except that a platinum wire mesh screen had replaced the stainless screen.

Another variation of the elution experiment was completed as follows. A weighed amount of centrifuged wet resin in a sample cell was contacted with TBP laden with 0.5 mole fraction each of uranium and thorium. The resin was loaded as in equilibration experiments. Next, concentrated HCl, 9.5 molar, was used to elute the resin. It was expected that only thorium would be eluted, and most of the uranium would form a chloride complex which would be readsorbed on the resin. The eluent was collected in batches of 50 mls and analyzed for thorium and uranium content.

To determine the effect of solution concentration on uranium adsorption from TBP two experiments were performed. In case one the total uranium content was set at approximately 21 millimoles concentrated solution in 500 ml and in case two (dilute solution the uranium concentration was 5.25 millimoles in 500 mls. A weighed amount of resin was contacted with these solutions until equilibrium was attained and the resin was then eluted using dilute nitric acid. The eluent was analyzed for uranium content as before.

PRESENTATION AND DISCUSSION OF RESULTS

As previously noted (see procedure), experiments were performed to determine the equilibrium amount of uranium adsorbed by the citrate type of resin from a 30 volume percent TBP Solution containing various concentrations of $UO_2(NO_3)_2$. The results of these experiments are shown in Figure 2. (These data are also tabulated in Table I of Appendix E.) The shape of the Figure 2 curve is not typical of equilibrium ion exchange experiments. Ion exchange resins have a definite ionic capacity, i.e. at equilibrium they will adsorb a fixed number of equivalents; this number is generally independent of the solution concentration. This result could be caused by a change in the valence of the uranium complexes adsorbed by the resin. However present evidence indicates that the uranium complex present in the TBP phase is $UO_2(NO_3)_2 \cdot 2$ TBP and that this form is independent of the $UO_2(NO_3)_2$ concentration as long as the TBP is in excess (3). It is also possible that the complex form within the resin might change its form and valence as the concentration of uranium within the resin phase varies. This possibility is examined further below.

Thus from figure 2 it is obvious that the mechanism of uranium sorption from TBP solution is not typical ion exchange. Further, Li and White (27) have shown that citrate form resin in contact with $UO_2(NO_3)_2$ in aqueous solution shows an apparent infinite distribution factor, D, where

$$D = \frac{\text{(equilibrium m. moles of uranium/gm dry resin)}}{\text{(equilibrium m. moles of uranium/liter of solution)}}$$

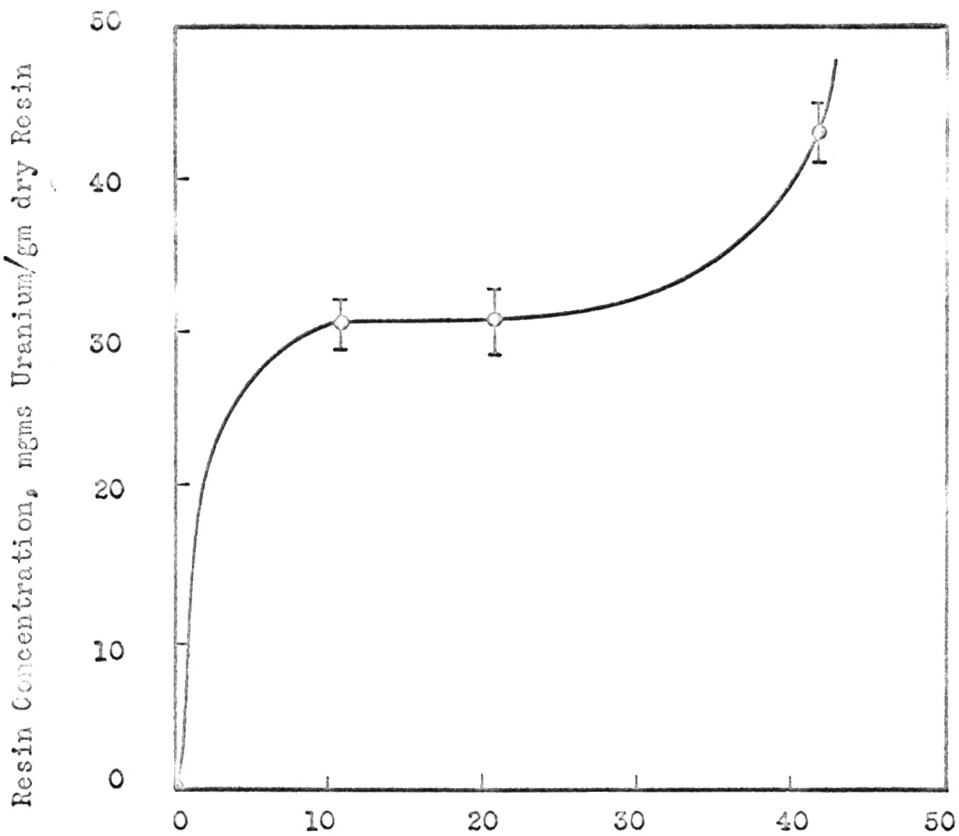

Figure 2 - Effect of TBP Soltion Concentration on The Amount of Uranium Sorbed

Thus, as in the case of adsorption from the TBP solution, the sorption process for the aqueous solution case is not typical ion exchange.

The equilibrium data obtained when contacting the water swollen citrate form Dowex 2 resin with TBP solutions containing mixtures of uranium and thorium nitrates, also exhibit a non-ion exchange character (see Figure 3(a)). As noted earlier (see Procedure for detailed description) the individual data points in Figure 3(a) were obtained by passing a uranium-thorium solution in TBP past water swollen resin until a state of equilibrium was attained. The total uranium-thorium concentration in the TBP was maintained at 21 millimoles per liter in all experiments, but the mole fraction uranium in the solutions was varied from zero to one. After equilibration the interstitial TBP solution was removed from the resin by centrifugation and the resin was then washed with distilled water. During the washing process a granular mixture of white and yellow precipitate formed at the surface of the resin particles. The yellow precipitate was typical of that found in basic (pH 7 or greater) solutions or uranyl ion, and the white precipitate was typical of that found in Th^{+4} solutions under similar basic conditions; subsequent chemical analysis of the wash solution confirmed the presence of both uranium and thorium. The uranium and thorium that formed this precipitate had apparently come from the interior of the resin particles (TBP solutions of uranium or thorium in contact with water do not form such precipitates and centrifugation at 300 g's leaves the resin particle surfaces essentially dry and free

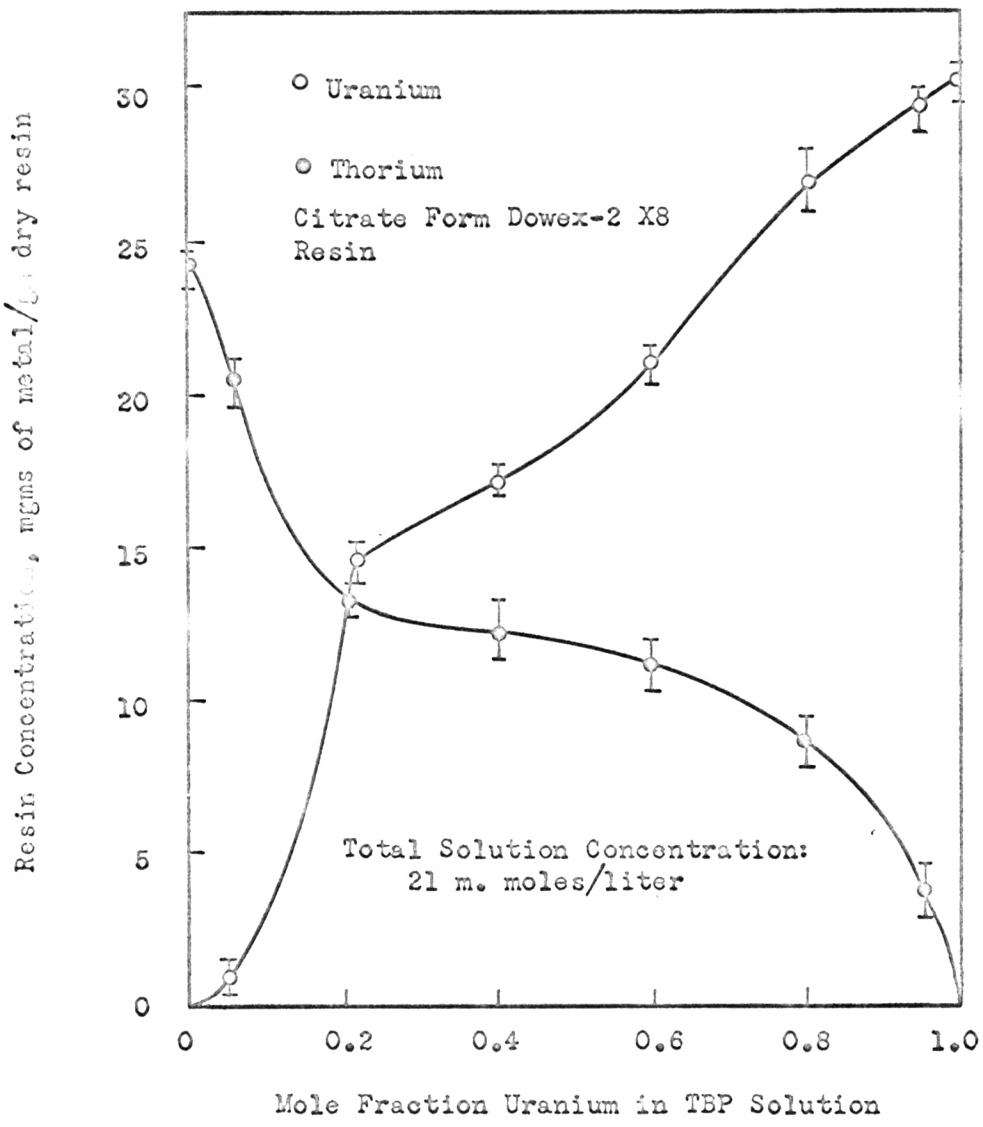

Figure 3(a) Uranium-Thorium-TBP-Dowex-2 X8 Equilibrium Curve

from adhering fluid). The fact that water containing no ionic species could wash uranium and thorium from the resin further establishes the non-ion exchange character of at least part of the adsorption of the two metals. This behavior of the resin is more typical of that found in the process of ion exclusion [18] where the sorbed species is attracted to and held by the resin phase by the forces important in physical adsorption.

The precipitate found during the washing process is believed to be result from hydrolysis induced by the presence of the strong base ion exchanger, Dowex 2. In effect the anion exchanger, acting as a strong base, produced a basic medium which gave rise to the hydrolysis of uranium and thorium salts. Thus the preciptate is believed to be a mixture of uranium and thorium hydroxides, which are known to be stable in neutral aqueous media [35]. However it is not possible to indicate the exact uranium and thorium salts hydrolysed. We would expect the following four species to be present in the solid resin phase citrate complexes of uranium and thorium formed in the resin and uranium and thorium nitrate salts, extracted from and held by the resin contained water. The types of citrate complexes present will depend on the pH and citrate to metal ratios in the resin. Since these ratios are difficult to determine it is not possible to predict the exact nature of the complexes. In addition, to further complicate the situation, it is possible that uranium and thorium may be partially present as their nitrate complexes.

The precipitate in the wash solution was dissolved by the addition

of a few drops of HNO_3 and the solution analyzed for uranium and thorium. The results of these analyses are shown in Table I. Large differences in values obtained in several cases for experiments 1 and 2 may have resulted from (1) incomplete washing and/or (2) from insufficient contact between the resin and TBP during the resin loading phase of the experiments. These possible sources of error will be discussed further following a presentation and discussion of the data shown in Figure 3(a).

Figure 3(a) shows the amounts of uranium and or thorium retained by the resin after the washing process just discussed. These data are also tabulated in Tables II and III. The results shown in Figure 3(a) also show a non-ion exchange character. If one adds the weights of uranium and thorium sorbed at the various uranium mole fractions it is found that this sum curve will pass through a maximum at about 0.8 mole fraction uranium. If the equilibrium were typical ion exchange, a straight line would connect the two ordinates of Figure 3(a). The equilibrium data of Figure 3(a) are redrawn in Figures 3(b) and 3(c) in terms of mole fraction metal in solution versus mole fraction metal in the resin.

In an attempt to explain the mechanism of uranium and thorium sorption leading to the data shown in Figure 2 to 3(c) as well as the formation of the precipitate in the aqueous wash, reference was made to the discussion of uranium-thorium citrate complexes presented earlier. The complexes of UO_2:Cit, ratio 3:2 postulated by Feldman et al (12) contradicts that presented by Heitner and Bobtelsky (17) who seemed to have identified a complex of the ratio 2:3. This shows the possibility of the existence of more than one anionic complex in the alkaline pH. Further, it could be

Table I - Uranium and Thorium in Wash Solution

Mole fraction thorium*	Thorium mgms/gm dry resin		Uranium mgms/gm dry resin	
	Expt. 1	Expt. 2	Expt. 1	Expt. 2
0	-	-	58.5	100
0.2	38.9	40.2	44.7	29.0
0.4	49.0	70.5	15.0	12.3
0.6	82.0	92.1	4.1	2.9
0.8	68.0	89.5	2.3	1.6
1.0	60.9	90.5	-	-

*Mole fraction in TBP uranium-thorium solution, total concentration 21 m. moles per liter of solution

Table II - Uranium in the Eluent

Mole Fraction Uranium in TBP*	Experiment 1 Uranium in mgms/gm dry resin		Experiment 2 Uranium in mgms gm dry resin		Average of two experiments, Uranium in mgms/gm dry resin	Experimental Error, % deviation from average
	Average of two analyses	Analysis Error, % deviation from average	Average of two analyses	Analysis Error, % deviation from average		
0	-	-	-	-	-	-
0.05	01.1	-	-	-	1.1	-
0.20	14.8	2.7	-	-	14.8	-
0.40	17.1	4.7	17.6	5.7	17.4	5.2
0.60	20.8	1.9	20.0	0.8	20.4	2.6
0.80	28.1	0.8	26.4	0.9	27.3	3.6
0.95	30.2	5.0	-	-	30.2	-
1.00	31.2	3.8	29.8	3.4	30.5	3.6

*Mole fraction in TBP uranium-thorium solution, total concentration 21 m. moles per liter of solution

Table III - Thorium in the Eluent

Mole Fraction Thorium in TBP*	Experiment 1 Thorium in mgms/gm dry resin		Experiment 2 Thorium in mgms/gm dry resin		Average of two experiments, Thorium in mgms gm dry resin	Experimental Error, % deviation from average
	Average of two analyses	Analysis Error % Deviation from average	Average of two analyses	Analysis Error, % Deviation from average		
0	-	-	-	-	-	-
0.05	3.66	2.1	-	-	3.66	-
0.20	9.14	1.0	7.60	1.3	8.37	9.2
0.40	10.0	0.8	8.42	3.2	9.22	8.6
0.60	11.1	1.1	13.3	0.8	12.2	9.0
0.80	13.0	-	12.2	2.8	12.6	2.9
0.95	20.4	1.9	-	-	20.4	1.9
1.00	23.2	2.4	25.4	2.2	24.3	4.5

*Mole fraction in TBP uranium-thorium solution, total concentration 21 m. moles per liter of solution

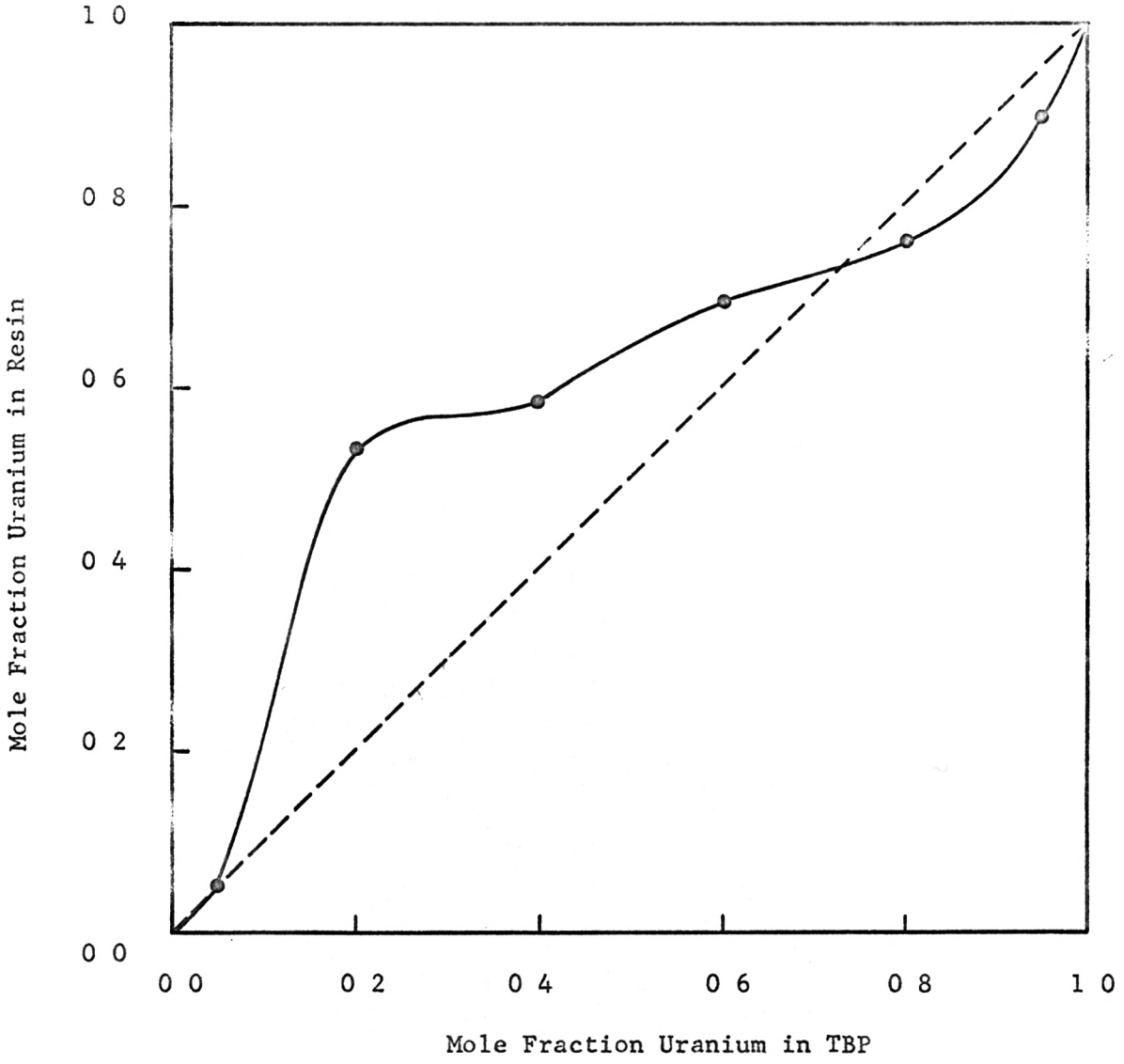

Figure 3(b) - Mole Fraction Uranium in TBP versus Mole Fraction Uranium in the Resin

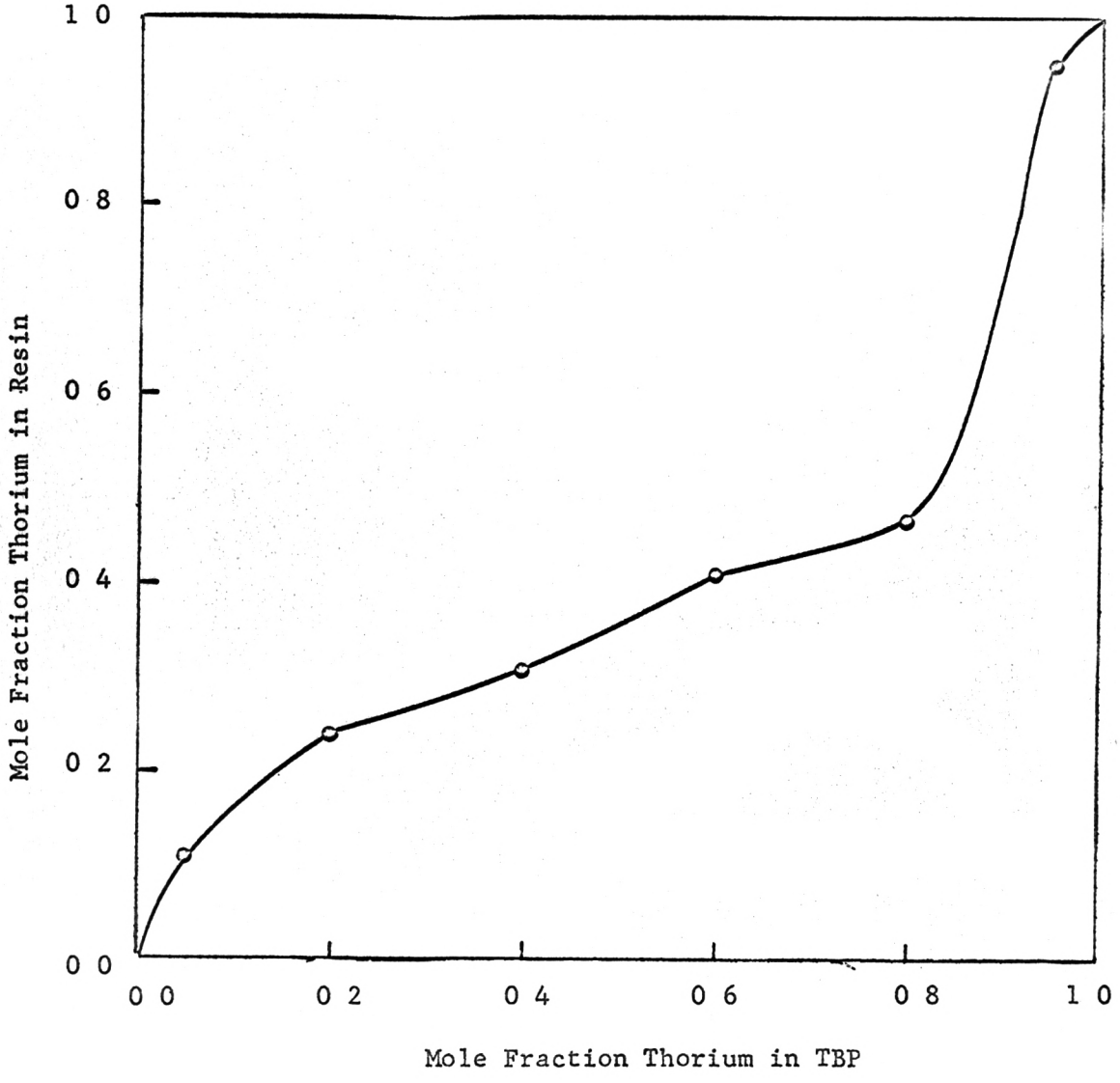

Figure 3(c) - Mole Fraction Thorium in TBP vs
Mole Fraction Thorium in Resin

expected that the proportion of these complexes present would vary with the concentration of uranyl ion in solution. When the concentration of uranyl ion is high compared with the citrate, we would expect an anionic complex of lower valence and consequently more adsorption of uranium per gram dry resin. This may be the cause of the variable capacity shown by the ion exchanger towards uranyl ion. In the case of thorium for the alkaline pH, the only information available is that of Bobtelsky and Grous (4) who postulate an anionic complex with valence 4 and with a thorium to citrate ratio 2:3. They do not report any hydrolysis of the thorium citrate in the alkaline pH. In the light of this information we would expect the resin to show a definite capacity for thorium (if present alone) in the alkaline media. However, when uranium too is present in solution, the variable uranium sorption capacity would be reflected in the thorium capacity as well.

Another important factor to be considered is the variation of distribution coefficient between TBP and water. Since TBP has a strong affinity for uranium it may not readily part with the uranyl nitrate when the latter is present in low concentration. Extraction of uranyl nitrate into resin might be further retarded if thorium nitrate too is present in solution. Since thorium has less affinity for TBP than uranium, it will be readily extracted into the resin phase and may act as a salting agent for uranyl nitrate. Opposed to this, since uranyl ion has a strong affinity for the citrate (27), it will attempt to get into the resin phase. Thus in the case of uranyl ion, adsorption will be due to two opposing affinities.

Again, from the shape of curves 3(a), 3(b), and 3(c), it is evident that either more than one complex ionic species is adsorbed or the mechanism of adsorption is not ion exchange. As already noted with regard to complex ionic species, it is possible that numerous species, of this type exist in the resin phase. Formation of the uranyl citrate and thorium citrate complexes will give rise to the accumulation of nitrate ions. These nitrate anions can not exist as free anions (due to the necessity for maintaining electroneutrality). They will either have to be adsorbed by the resin as simple nitrate ions or if they are present in sufficient concentration will combine with uranyl and thorium ions to form nitrate complexes which in turn will be adsorbed by the resin. With regard to a non-ion exchange mechanism of sorption, Helfferich (18, p. 217) notes that when the solution concentration of a sorbed species becomes equal to or greater than the concentration of ion exchange sites within the resin, a process of "invasion" occurs, i.e. the undissociated electrolyte or complex present in solution will be absorbed or adsorbed by the resin. If the process is absorption, the resin phase is merely acting like a sponge; if the process is adsorption then some attractive force will exist between the sorbed species and the resin (this latter situation would be, or would be similar to, the process known as electolyte or ion exclusion (18, p. 132)).

The possibility of existence of several complex species in the ion exchanger together with the fact that sorption could be due to <u>invasion</u> makes a definite mechanistic analysis of the process difficult if not impossible. A systematic analysis would require a knowledge of the

activity coefficients for the various species present (18); such activity data are extremely difficult to obtain in mixed electrolyte systems. However activity coefficient data alone would reveal little about the types of complexes present and thus even with this information available an exact mechanism could not be described.

As seen from the TBP equilibration data, since both uranium and thorium are adsorbed by the resin, the only way these metals could be separated is by using a suitable eluent. As already indicated in the section, Elution of Uranium And Thorium From Resin, it was expected that concentrated hydrochloric acid would be a good choice as an eluent. Since thorium does not form any chloride complex but uranium does, thorium alone would be eluted by the concentrated hydrochloric acid. To examine this choice, two elution experiments were carried out.

In one experiment 250 mls of an aqueous solution of uranium-thorium mixture and also containing 9.5M HCl was passed over the citrate form of Dowex 2 resin. The effluent collected in 50 ml batches was analyzed for uranium and thorium. Table IV shows the results of these analyses. It is seen from this table that thorium is not sorbed by the resin in concentrated HCl media and, as expected, uranium is. The uranium chloride complex held by the resin was readily eluted by dilute nitric acid and this eluent was analyzed. No trace of thorium was found in this eluent although uranium adsorption was found to be as high as 95 mgms/gm dry resin.

In another variation of the elution experiment the resin was first loaded from a TBP solution of uranium-thorium mixture (0.5 mole fraction each, total concentration 21 m moles per liter). Then 250 mls of concen-

Table IV - HCl Loading-Elution Data From Aqueous Mixture of Uranium and Thorium

Weight of wet resin used = 4.32 gms

Total molarity of the Solution = 4 m.moles in 250 c.c.

Mole fraction uranium = 0.75

Molarity of HCl = 9.5

Total uranium in the eluent = 242 m grams

No. of 50 ml Batches Fed	Uranium and Thorium in Feed Solution, mgms per batch		Uranium and Thorium in Effluent, mgms per batch		Thorium Adsorbed in Resin, mgms per batch	Uranium Adsorbed in Resin, mgms per batch
	Uranium	Thorium	Uranium	Thorium		
1	170	50	105	50	-	65.0
2	170	50	91.5	50	-	78.0
3	170	50	92.5	50	-	79.5
4	170	50	128	50	-	42.0
5	170	50	170	50	-	-

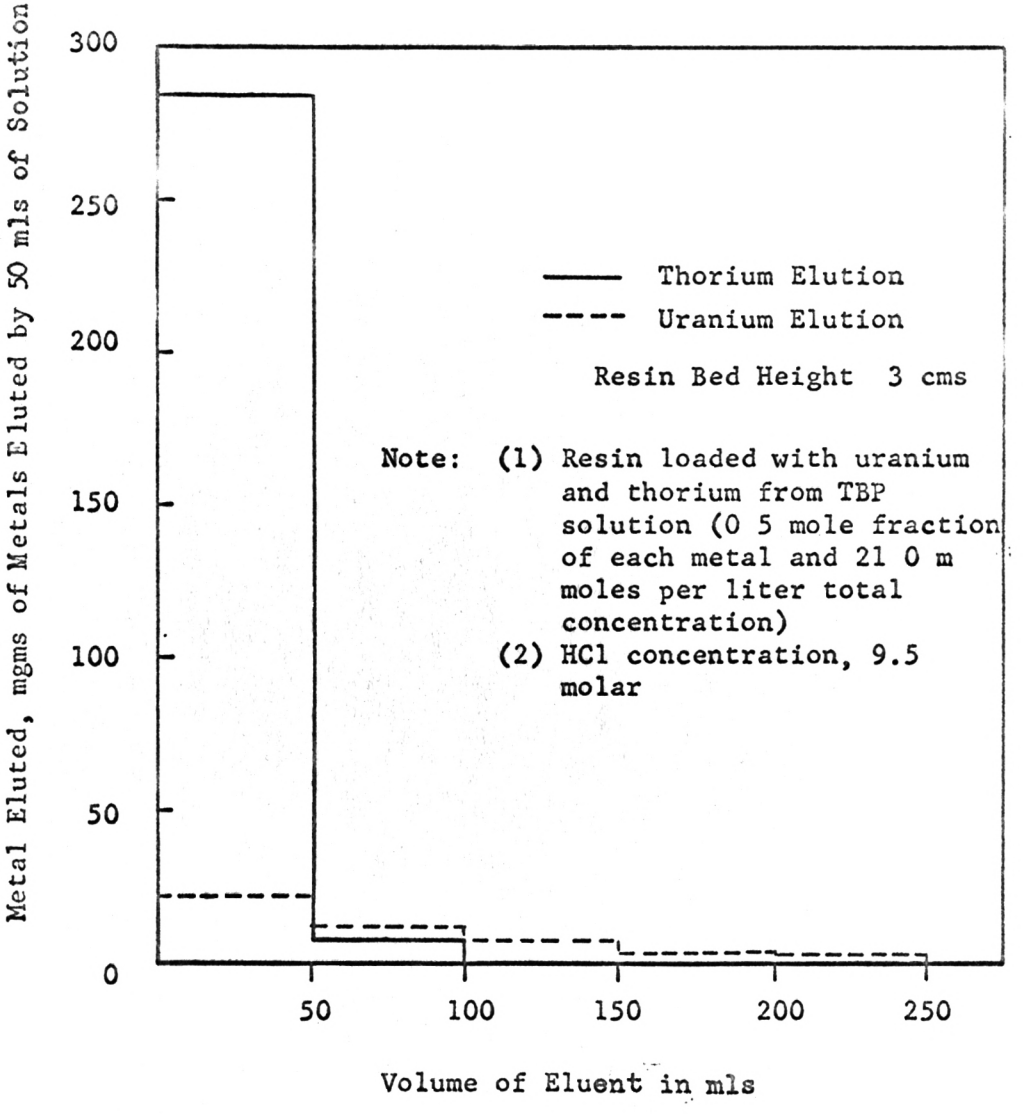

Figure 4 - Concentrated HCl Elution Curve

trated HCl (9.5M) was passed through the resin bed as the eluent. As before the eluent was collected in 50 mls batches and analyzed for uranium and thorium. Figure 4 is a plot of the elution data obtained from this experiment (The analyses report is also presented in Table II of Appendix E). From the elution curve, it can be concluded that thorium is almost completely eluted in the first 50 mls whereas uranium is readsorbed on the resin as the chloride complex and only a few milligrams is eluted in each 50 mls. It is probable that if any barren citrate resin were present in the bottom of the bed even the small amount of uranium lost in the experiment cited above would also be taken up and a complete separation of the thorium from uranium would be achieved. The uranium-chloride complex was later eluted from the resin with dilute HNO_3 and the eluent analyzed. In this case the uranium adsorbed as the chloride complex was found to be completely free of thorium.

Error Analysis

The nature of the equilibration experiments and analytical procedures adopted in describing the various equilibration and dynamic elution data did not preclude the presence of errors. In analyzing the errors present, two types of errors were considered, (1) errors in chemical analysis and (2) experimental errors which would include the analysis as well as other errors. The errors in chemical analysis were estimated by performing each chemical analysis twice. The experimental errors were estimated likewise by repeating each of the various experiments twice. Both types of errors are reported in Tables II and III. In no case was the experimental error greater than 10 percent; the average experimental error was less than 4.5 percent. The average error in carrying out thorium analysis was 1.8 percent while the average uranium analytical error was 3 percent.

The chief contributions to the analytical error were loss of uranium or thorium either during the transfer of precipitates or the evaporation of the various solutions. Both of these errors would lead to too low values; on the other hand incomplete ignition of the thorium or uranium precipitates would lead to too high values.

Experimental errors noted other than the analytical error include non-uniformity of the resin; variations of resin capacity of the order of 1.5 percent per gram are common. Since from 2 to 4 grams of resin were used in the various experiments, errors of up to 6 percent could have been introduced in this manner. In this same regard, as noted earlier, an error of 1.7 percent existed in the determination of the weight of dry resin (from the weight of wet resin) used in each experiment. The combination of the error in resin capacity plus error in weighing could lead to an average error of 2.27 percent per dry gram. The fact that varying amounts of resin were used could also have introduced variations in the character of the washing, centrifugation and resin loading and eluting procedures. These variations may have contributed to variences found in the final results.

It was noted earlier that large discrepancies exist in the wash solution data shown in Table I. This may be due to a difference in contact time leading to more concentration of material in the resin by the process of invasion. This material is loosely held and is easily washed out. Other sorbed species in the resin are more strongly attached to the resin phase and are not washed out; if one examines the data in Tables II and III or Figures 3(a), 3(b) or 3(c), one notes small errors in these results (on the average 4.5 percent). Thus the large errors in wash data could not be due to the washing out of more material in one experiment than the other although the amount of material in contact with the resin after TBP contact was the same initially. This amount

of material in the resin after TBP contact must have varied considerably. Some of this was lightly held by the resin and easily washed out; a reproducible amount was more strongly held and could only be removed by elution with dilute HNO_3.

CONCLUSIONS

From the equilibration and concentrated HCl elution data it is concluded that the modification in the Thorex process is technically feasible. However further studies to determine the exact contact time required in each stage of the process would be required. In the studies presented here, equilibration times of 6-7 hours were provided. An extended contact time would necessitate prohibitively large equipment in an actual processing plant and shorter contact times would thus be called for. If the kinetics of resin loading from TBP, and resin elution by concentrated HCl and dilute HNO_3 are such that contact times of the order of a few minutes to 30 minutes are possible, practical modifications in the Thorex process could be effected as shown in Figure 5.

In the modified process, TBP extractant obtained from column I and containing uranium and thorium would be contacted countercurrently with citrate type Dowex 2-X8 anion exchanger. The loaded resin would next be passed to an elution column where the thorium would be eluted by concentrated HCl. Uranium would then be separately eluted in another section of the same column using dilute nitric acid. Fresh resin would be added to the top of the thorium elution column so that uranium-chloride complex would be adsorbed and would not escape with the thorium.

Further studies on a bench scale would be necessary before considering the above modification for a large scale processing plant. Also, an economic evaluation of the modification is essential. Such an evaluation without the kinetics data is beyond the scope of present work.

However an estimate of the quantity of materials required to process a 1 to 1 uranium-thorium fuel mixture per kilogram of fuel is presented in the following table.

Table V

Required Quantities of Process Materials

Per Kilogram of Fuel *

	Material	Quantity (in liters)
1)	30 volume percent TBP[1]	200
2)	citrate form of water swollen Dowex 2-X8 resin[2]	44
3	concentrated Hydrochloric acid (9.5M [3]	100
4	dilute nitric acid[4]	44

*Note ratios of the quantites described in 1 through 4 above give the operating line slopes in the various process units.

1. Metals concentration of 21 m. moles liter of TBP was assumed.
2. Resin capacity assumed was 90 percent of the equilibrium value with 1 1 mixture at 21 m. moles per liter total concentration.
3. 90 percent utilization of concentrated HCl was assumed.
4. 90 percent utilization of dilute HNO_3 was assumed.

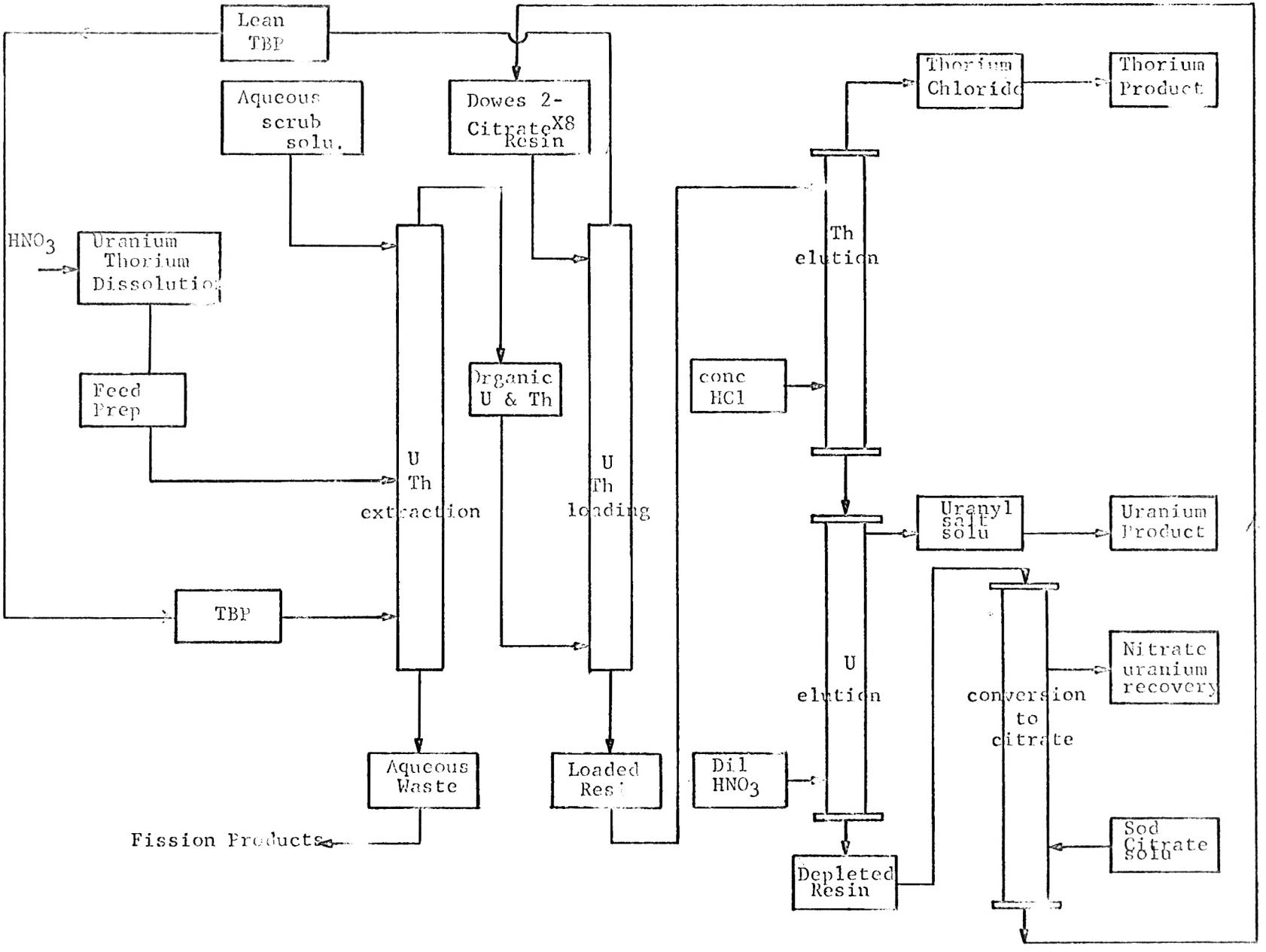

Figure 5 - Modified Thorex Process Flow Diagram

FUTURE WORK

Preliminary equilibrium data have been determined for the systems TBP-uranium - Dowex 2-X8 citrate form resin and TBP-uranium-thorium - Dowex 2-X8 citrate form resin. The uranium system has been investigated up to a total concentration of 42 milimoles per liter while the mixed uranium-thorium system was investigated up to a total concentration of 21 milimoles per liter. It would be of interest to determine additional equilibrium data for both these systems at higher concentrations. In highly enriched U-233 systems work at concentrations greater than about 10.2 gms/liter in TBP or 20.8 mgms/gm dry resin would require that all process equipment used in applying these systems to an actual separation problem be designed to prevent critical mass accumulations See Appendix F).

It has been noted that the process of ion exclusion or processes of a similar nature may play some part in the uptake of both uranium and thorium by the resin. If such a mechanism plays a part in the metal uptake it would be expected that as the water content of the resin increased the extent of metal sorption by the resin would be increased. One method of increasing resin water content is to lower the resin cross linkage. It would be of interest to determine the extent of uranium and thorium sorptions at several fixed concentrations in resins of different cross linkage. Such data may provide additional insight into the mechanisms of uranium and thorium sorptions from TBP solution.

As noted, future application of the data collected here will require the determination of column kinetics data. Necessary data would include

transfer unit heights for uranium and thorium mass transfer from TBP to the resin and for the separate elution of the two metals from the resin. It will also be of interest to determine if it is possible to separate and sorb uranium chloride complex from solution onto the resin during the thorium elution process.

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APPENDICES

Appendix - A

Properties of the Dowex 2-X8 Resins

Nature - Strongly Basic Anion Exchanger. (Dimethyl Ethanol Benzyl Ammonia)

Cross-linkage - 8.

Ionic form as shipped - Cl^-

Physical form - Spheres.

Mesh Size - 20-50 U.S. Screen Size

Shipping density (lb/ft^3) - 44

Moisture content (percent) - 37.

Volume change (percent) $Cl^- \longrightarrow OH^-$ = +14%

Effective pH Range - 0-14.

Selectivity - Cl^-/OH^- = Approximately 1.5

Order of selectivity for Ions - $I>NO_3>Br>Cl>OH>Acetate>F$

Total Exchange capacity - (Cl^- -form)

- Kgm as $CaCO_3/ft^3$ - 29.0
- Meqs/gm dry Resin - 3.5
- Meqs/ml wet Resin - 1.33

Sphericity (percent) -$>$85

Bed expansion - 50 percent maximum at 2gpm/ft^2 at 25^oC.

Pressure drop - Approximate 0.5 $lb/in^2/ft$ at 5 gpm/ft^2.

Stability

Thermal - (OH^- form - Fair up to 30^oC)

(Cl^- form - Good up to 150^oC)

Solvent - Very Good

Oxidation - Slow in hot 15 percent HNO_3

Reduction - Breakdown in presence of some sulfur containing reducing agents.

Appendix - B

Procedure for Quantitative Determination of Thorium Using Thorin Indicator

The spectrophotometric calibration Chart, Figure 6, covering the thorium concentration range from 0.3 - 10 gms/ml was constructed as follows Solutions of known thorium content were placed in a 50 ml volumetric flask. Then 7 mls of 0.1 percent strength thorin indicator solution and 1 ml of concentrated HCl were added and the volume made up to 50 mls. The pH of the solution was in the neighborhood of 1 as required. The solution was placed in standard spectrophotometric sample cell and the transmittance measured at 545 mμ by means of Nuclear Engineering's Beckman Spectrophotometer (Serial No. 261243). The blank test solution used as a reference condition was made of 7 mls of Thorin Indicator and 1 ml of concentrated HCl in 50 mls total volume.

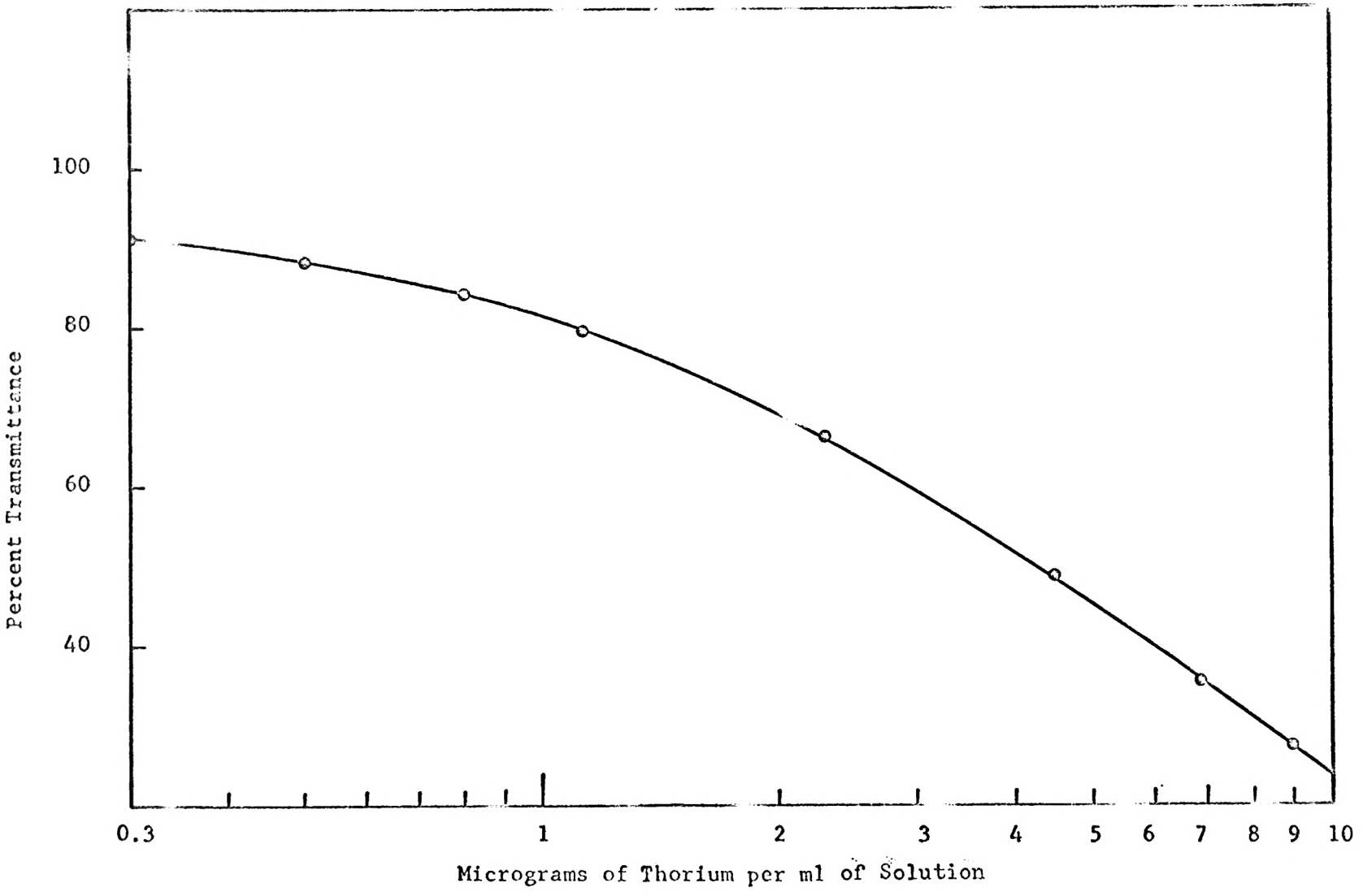

Figure 6 - Spectrophotometric Thorium Estimation Curve

Appendix - C

Spectrophotometric Method for Urnaium Determination in Aqueous Media

The yellow colored uranyl nitrate solution shows adsorbancy at 420 mμ and obeys Beer's law in the range 0.005 to 0.030 grams/ml of solution. Hence, this method is applicable for uranium determination in the milligram range. As the eluent to be ana yzed for uranium was known to contain nitric acid the blank for the transmittance measurements also contained 5 mls of concentrated HNO_3 in 100 mls of the solution. The uranium calibration chart is shown in Figure 7.

To check the purity of analytical grade uranyl nitrate supplied by the Fisher company, the salt was standardized against high purity National Bureau of Standards U_3O_8. For this standardization, a known weight of U_3O_8 was dissolved in nitric acid and the volume made up to 100 mls. By measuring the transmittance of this latter solution at 420 mμ a calibration chart was constructed. Uranyl nitrate solution of known strength prepared from Fisher reagent was checked against this calibration curve. The Fisher salt was found to conform with the formula $UO_2(NO_3)_2 \times 6H_2O$.

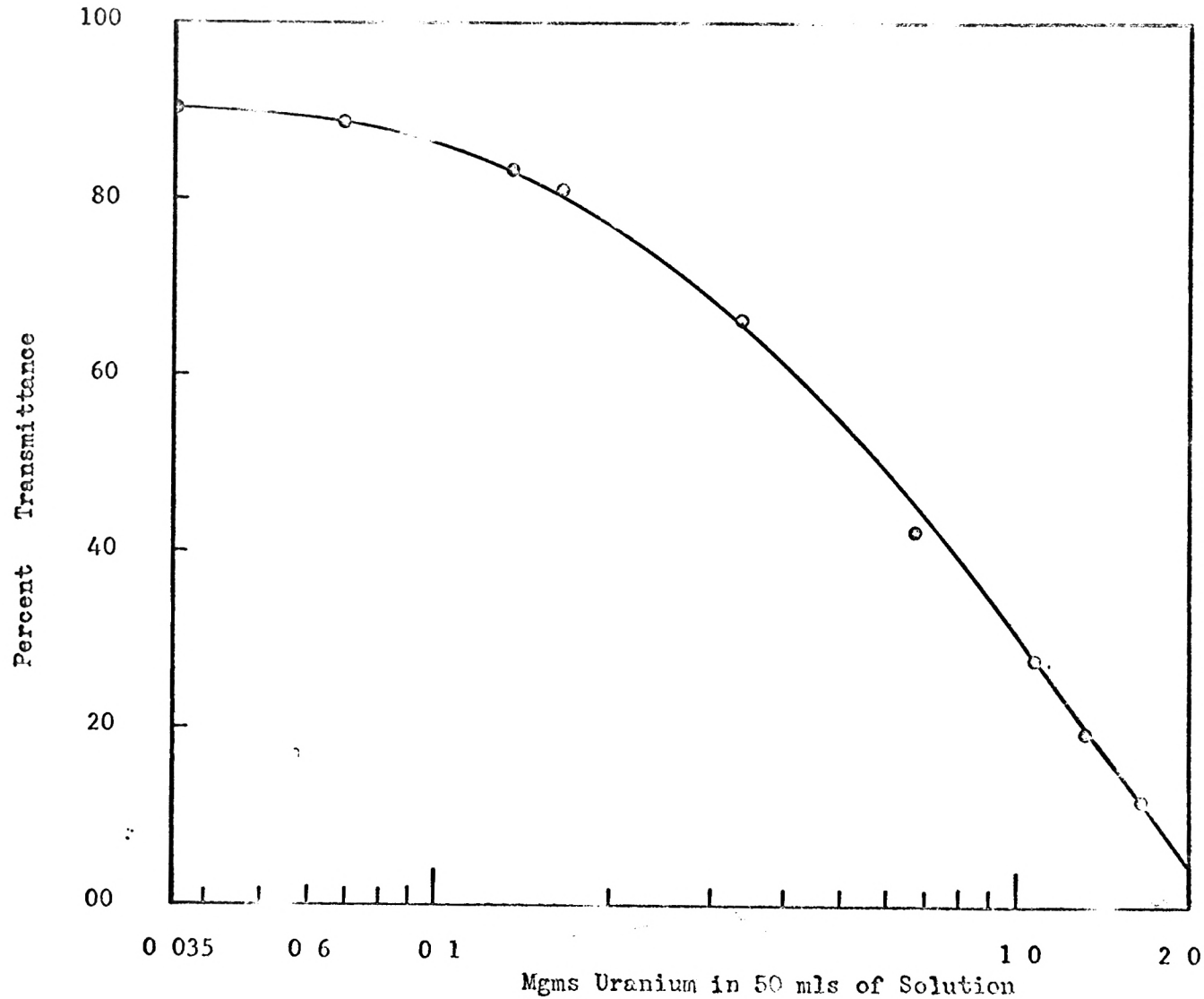

Figure 7 - Spectrophotometric Uranium Estimation Curve

Appendix - D

Gravimetric Estimation Method for Thorium and Uranium

A known volume of the thorium solution was diluted to about 150 mls and heated to boiling. The hot solution was transferred to a polyethylene beaker and a few drops of HF were added; the solution was then allowed to stand for 24 hours. After the 24 hour aging period the flouride precipitate was filtered and ignited in a platinum crucible; once constant weight was attained, the sample was weighed as ThO_2.

The filtrate resulting from the thorium determination was acidified with sulphuric acid and placed in a platinum evaporating dish. After evaporation to dryness (to remove hydrofluoric acid) the residue was dissolved in 100 mls of water to which a few drops of HNO_3 and ammonium nitrate were added. The solution was heated and a slight excess of ammonia was added. The solution was heated again until the smell of ammonia disappeared. The precipitate, Ammonium diuranate, was filtered, washed with water containing ammonium nitrate, ignited and finally weighed as U_3O_8.

Appendix - E

Table I - Effect of TBP Solution Concentration on the Amount of Uranium Sorbed

Wr. of wet resin used	Total Uranium Molarity in TBP Solution	Uranium Estimated in the Eluent mgms/gm dry Resin		Uranium Estimated in Wash mgms/gm dry Resin	
		Analysis I	Analysis II	Analysis I	Analysis II
4.96	10.5 m. moles per liter	31.3	29.1	-	77
4.27	21 m. moles per liter	30.7	29.8	-	100
5.14	42 m. moles per liter	43.2	43.1	-	108

Appendix - E

Table II - Concentrated HCl Elution Data

Weight of wet resin used = 5.55 gms

Organic Solution of total molarity 21.0 m. moles/liter

with 0.5 mole fraction each of Uranium and Thorium

Quantity of uranium eluted from resin = 69.6 mgms (total)

No. of 50 ml Batches Fed	Thorium in mgms		Uranium in mgms
	Analysis I	Analysis II	
1	275 mgms	260 mgms	23.1 mgms
2	2.96	-	11.4
3	nil		7.0
4	nil	-	5.9
5	nil	-	5.0

Appendix - F

Calculation of Critical U-233 Concentration in Various Systems At Infinite Volume

a) To calculate the minimum concentration of uranyl nitrate (U-233 in water that can form a critical mass at infinite volume it is assumed that the uranium is present in the form $UO_2(NO_3)_2$ and that the following equation applies (39).

$$k_\infty = \eta\varepsilon pf = 1 \text{ (at critical condition)} \qquad (1)$$

Where

ε = fast fission factor

p = resonance escape probability

f = thermal utilization factor

η = yield of fast neutrons per thermal neutron captured in fuel

The adsorption cross-sections shown in the fo lowing tables were used in the calculation of the thermal utilization factor.

Material	Adsorption Cross-reaction in barns	Moles/Mole of U-233
U-233	590	1.
Nitrogen	1.88	2.
Water	0.66	y.

Then

$$f = \frac{590}{590 + 2 \times 1.88 + 0.66y} \qquad (2)$$

For U-233 the value of η is 2.31 and then assuming $p=\varepsilon=1$ and substituting equation 2 in equation 1 we have

$$\frac{2.31 \times 590}{590 + 3.8 + 0.66y} = 1$$

Solving for y we find that y = 1150 gm moles water per mole U; hence the maximum concentration of U-233 per liter of solution is

$$\frac{233 \times 1000}{1150 \times 18}$$

$$= \underline{11.3 \text{ gms/liter}}$$

b) To calculate the minimum concentration of uranyl nitrate (U-233) in TBP that can form a critical solution at infinite volume it is first necessary to calculate the microscopic adsorption cross-section of TBP. The chemical formula of TBP is $(C_4H_9)_3PO_4$, taking one molecule as the basis

$$\sigma_{TBP,\ molecule} = 12\sigma_C + 27\sigma_H + \sigma_p + 4\sigma_O.$$

The following adsorption cross-sections were used.

Material	Adsorption Cross-Sections In Barns
carbon	0.0037
hydrogen	0.33
phosphorus	0.2
oxygen	0.0020

Hence, $\sigma_{TBP,\ molecule} = 0.0037 \times 12 + 27 \times 0.35 + 0.2 + 4 \times 0.0002$

$= 9.14$ barns.

Now, calculating the thermal utilization factor as in the aqueous case,

$$f = \frac{590}{590 + 2 \times 1.88 + 9.14\ y}$$

where y = number of moles of TBP/mole of U-233

For the critical condition then

$$\frac{2.3 \times 590}{590 \times 2 \times 1.88 + 9.14\ y} = 1$$

Solving for y,

$$y = 83.3 \text{ moles/mole U}$$

Now, since the density of TBP is 0.97 gms/ml and the molecular weight is 266, the permissible concentration of uranium per liter of TBP solution is

$$= \frac{233 \times 0.97 \times 1000}{83.3 \times 266} \text{ gms/liter}$$

$$= 10.2 \text{ gms/liter}$$

$$= 43.7 \text{ m. moles/liter}$$

c) To calculate safe concentration of uranium in the resin, a single resin "unit molecule" of chemical formula $C_{11}H_{17}NO$ was considered. The molecular weight corresponding to this formula = 179. Using the procedure applied to the TBP molecule the thermal neutron adsorption cross-section is 7.35 barns/unit molecule. Now, taking a basis of 1 ml of the water swollen resin and assuming the water swollen capacity of the resin is 1.4 meq/ml, the number of resin "unit molecules" per cm^3 is

$$= 1.4 \times 10^{-3} \times 6.02 \times 10^{23}$$

$$= 9.4 \times 10^{20}$$

Water content per cm^3 of wet resin is 0.37 gms;* then the number of molecules of water cm^3 is

* (Also assumed to include water in voids in the resin bed)

$$= \frac{0.37}{18} \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{cm}^3}$$

$$= 123 \times 10^{20} \frac{\text{molecules}}{\text{cm}^3}$$

$$\text{Mole fraction of resin} = \frac{8.4}{131.4} = 0.06$$

$$\text{Mole fraction of water} = \frac{123}{131.4} = 0.940$$

The average molecular weight of the water swollen resin is then

$$= 0.06 \times 179 + 0.94 \times 18$$

$$= \underline{28.2}$$

The average microscopic cross section is then

$$= .06 \times 179 + 0.94 \times 0.66$$

$$= \underline{1.094 \text{ barns}}$$

To complete the calculation for the critically limiting uranium (present as $UO_2(NO_3)_2$) concentration at infinite volume, equation 1 is again applied and the limiting ratio of resin to uranium is found to be 697 or in terms of gms per liter of wet resin

$$= \frac{1}{697} \times \frac{233}{28.2} \times 0\ 705 \frac{\text{gms}}{\text{ml}} \times \frac{1000 \text{ mls}}{\text{liter}}$$

$$= 8.35 \frac{\text{gms uranium}}{\text{liter of wet resin}}$$

$$= 35.0 \frac{\text{m moles}}{\text{liter of wet resin}}$$

$$= 20.8 \frac{\text{mgms}}{\text{gm dry resin}}$$

SEPARATION AND PURIFICATION OF URANIUM AND THORIUM FROM ORGANIC LIQUIDS ON AN ANIONIC EXCHANGE RESIN

BY

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D.I.I.Sc., Indian Institute of Science, India, 1958

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Approved by:

Major Professor

Abstract

With the advent of thermal breeders, uranium-thorium mixtures as the reactor fuel and also the necessity for processing such irradiated fuel mixtures, will become more common place. The existing Thorex process, based on liquid-liquid extraction, for the separation of reactor fission products and uranium and thorium is beset with problems. In order to overcome some of the drawbacks of the existing process and also to improve it by reducing the plant volume and simplifying the process flow sheet, the application of the GLX concept to uranium-thorium separation is studied in this thesis. In an attempt to eliminate two scrubbing sections of the Thorex process and to replace them with a compact counter-current ion exchanger, the data pertaining to the system uranium-thorium-TBP-citrate anion exchange resin, was collected. The equilibrium amount of uranium and thorium adsorbed by a citrate type of water swollen resin from a TBP solution of uranium-thorium mixture, of total molarity 21 m. moles/liter and uranium concentration varying from 0 to 1.0 mole fraction, was determined experimentally. The amount of uranium sorbed varied from 0 to 30.5 mgms/gm dry resin; under the same conditions the amount of thorium sorbed varied from 24.5 to 0.0 mgms/gm dry resin.

The loaded resin when washed with distilled water was found to hydrolyze a portion of the sorbed uranium and thorium; the hydrolyzed species were then present as precipitates. The uranium content of this precipitate varied from 0 to 100 mgms and thorium content from 90 to 0 mgms.

Studies on the effect of variation of total uranium solution molarity on the amount of uranium adsorbed from TBP solution indicated that at

still higher concentrations than those studied here (maximum of 42 m. moles per liter of TBP solution) more uranium would be adsorbed. For TBP solutions containing uranium concentrations varying from zero up to the maximum, the weight of uranium sorbed by the resin varied from zero to 43.2 mgms/gm dry resin. Further the uranium estimated in the wash solution of these experiments showed a maximum of 77 to 108 mgms/gm dry resin.

Since both uranium and thorium were adsorbed by the resin, it was necessary to devise a means of selectively eluting thorium; the application of concentrated HCl as the thorium eluent was studied. When an aqueous solution of uranium-thorium mixture containing 9.5 M HCl was passed over a loaded resin (previously loaded with uranium-thorium mixture from a TBP solution), thorium was quantitatively eluted while the bulk of the uranium was retained by the resin.

Based on the equilibrium and HCl elution data it was concluded that modification of the existing Thorex process can be effected. The modifications suggested and the altered process flow sheet are presented in this thesis. In the altered flow sheet two scrubbing sections are eliminated and replaced by a counter current ion exchanger containing loading and eluting sections. Since the stage heights in the ion exchange system are expected to be lower than those found in liquid-liquid extraction, a reduction in the size of the process ng plant is expected. Concentrated HCl (9.5 M) is recommended as the eluent for thorium and dilute HNO_3 (0.5 N) is recommended for uranium recovery.

An evaluation of several possible methods for uranium and thorium

chemical analysis are presented. Gravimetric methods based on thorium flouride and ammonium-diurnate precipitation were selected as the most reliable methods when both uranium and thorium are present in the same solution.